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Development of an innovative marine monitoring system for CO₂ leaks: system design and testing

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Abstract

A critical component of long term geological sequestration of anthropogenic CO₂ will be our ability to adequately monitor a chosen site to ensure public and environmental safety. Near surface monitoring is particularly important, as it is possible to conduct sensitive and direct measurements at the boundary between the subsurface and the biosphere (i.e. surface water or atmosphere). While discontinuous surface monitoring is often performed, continuous monitoring is preferable if one hopes to observe a leak in its early stages to allow for rapid remedial action. The geochemical signal that may result from a near-surface CO₂ leak might take the form of increased soil gas concentrations (on land) or changing pH, Eh, and aqueous chemistry (in groundwater or surface water), and thus continuous monitoring stations capable of analyzing for these parameters have great potential for early leak detection. In the framework of the EC-funded CO₂GeoNet and CO₂ReMoVe projects innovative monitoring systems have been designed and constructed for autonomous deployment in marine environments above geological CO₂ storage sites. The system developed within CO₂GeoNet was tested at a site in the Gulf of Trieste where there is no gas release; this site was chosen due to easy access and the presence of an existing oceanographic buoy onto which the monitoring station was mounted. Tests on this early prototype highlighted the various difficulties of working in marine environments, and this experience formed the basis for a new system developed for deployment at the Panarea test site within CO₂ReMoVe. This second site is located off the coast of Panarea Island, to the north of Sicily, where naturally-produced CO₂ leaks from the seabed into the water column. The advantage of this site is that the leaks occur in a relatively near-shore environment (<300m) and in water that is not too deep (<25m), thereby allowing for easy access by SCUBA divers for system testing and maintenance. This location allowed the unit to be connected via cable, rather than a buoy, which makes power supply and data transfer simpler. The system developed for this site consists of three monitoring points that are connected to a land-based control unit. Each point, located 100, 200, and 300m from shore in different CO₂ flux regimes, is able to measure dissolved CO₂ and CH₄, conductivity, pH, and temperature using low cost but sensitive sensors. The complete system consists of flexible solar panels, a central control unit and three monitoring points, and data download is conducted using a GPRS connection and a web server. Difficulties with the initial deployment in early April of 2008 has necessitated further development work, with the second deployment planned for early November. The following paper discussed the experience gained with these stations, and presents data analysis and anomaly recognition from a land-based monitoring station that has been collecting dissolved CO₂ data for over 18 months.

© 2009 Elsevier Ltd. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).marine monitoring station; dissolved CO₂; Panarea; CO₂ geological storage

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1. Introduction

The monitoring of CO₂ geological storage sites will be a critical component for carbon credit auditing and for convincing stakeholders and the public at large that these sites are safe. There is an extensive toolbox of monitoring techniques that can be used at these sites. Many of these are existing methods that were developed for deep oil exploration and exploitation (e.g. 4D seismic), for mineral exploration (e.g. EM), or for environmental surveys (e.g. remote sensing). One approach that has been receiving particular attention over the last number of years involves the use of autonomous geochemical and/or geophysical monitoring systems. Although such stations have been used for a number of years for groundwater monitoring, agricultural studies, or physical oceanography studies, to name just a few, recent advances in sensor miniaturization, decreased power consumption, and wireless data transfer have made the deployment and use of such systems more attractive for large-scale or remote CO₂ storage monitoring. Due to the flexibility of design possible with such stations, there is the potential to use them to check for leaks from a CO₂ geological reservoir in a number of different environments, such as deep or shallow aquifers for changes in dissolved CO₂ concentrations or water chemistry, the vadose zone for increased CO₂ or tracer gas concentrations, or in marine environments for modified physical-chemical parameters. This last is particularly challenging considering the corrosive nature of seawater, the potentially high pressures, and the fact that these sites will likely be isolated and far from installations or power supplies.

Numerous, relatively-inexpensive, commercial systems exist on the market for on-shore monitoring of CO₂, based primarily on IR sensors. However because of the greater complexity of a marine application, far fewer systems are available for off-shore environments and these tend to be quite expensive. This high cost limits the number of units that can be deployed, which in turn limits the potential for identifying a CO₂ leak from the seafloor. To overcome some of these difficulties we have developed various in-house systems that has allowed us to decrease unit costs while at the same time providing more flexibility. The present article details experience gained in developing these remote geochemical stations for monitoring groundwater and marine systems above CO₂ geological storage sites, work conducted during the EC-funded Nascent, CO2GeoNet, and CO2ReMoVe projects.

2. Previous experience

Initial experience in a marine environment was gained during a joint research project within the Network of Excellence CO2GeoNet. During this research a geochemical monitoring station was developed (together with network partners OGS and BGR) for free and dissolved gases (CO₂ and CH₄), and then subsequently deployed for testing in the Gulf of Trieste, northern Italy (Fig. 1). For this application our group used a “hybrid” approach,

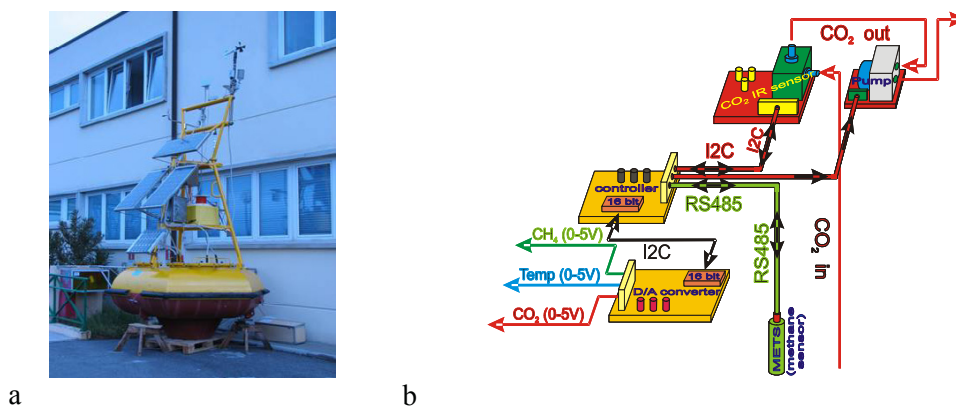


Figure 1. The Trieste monitoring system consists of an external part, mounted in a buoy, and a remote part with the undersea sensors. The buoy houses the power supply, system control cards and data storage unit (a). The Sapienza part of this system was dedicated to the remote part, including analysis of dissolved CH₄ (Capsium METS® commercial probe) and dissolved CO₂ (in-house made part the system). Dissolved CO₂ is measured by pumping air through a gas-permeable membrane and analysing it with an IR sensor installed on the buoy (b).

whereby both commercial (dissolved CH_4) and in-house (dissolved CO_2) devices were used. Field testing of the system between October 2006 and June 2007 highlighted areas in which the system could be improved for the challenging marine environment. Based on these results a different approach was used for a subsequent marine monitoring system, developed within the CO_2ReMoVe project and initially deployed at the natural test site off Panarea Island, southern Italy. Here naturally-produced CO_2 is leaking from the sea-bed into the overlying water column, thereby producing a “natural analogue” of a leaking CO_2 storage site where marine monitoring technologies can be tested.

Below we will discuss the development, testing, and recent deployment of the Panarea system. Because of problems with the initial deployment in April there is limited data available from this station, thus results from an on-shore, groundwater system at Camaiole (central Italy), that has been installed for over a year and which has a configuration similar to the Trieste system, will be discussed in the context of data analysis and the statistical recognition of temporal trends and anomaly recognition.

3. The Panarea monitoring system

3.1. System Setup

The new, totally in-house created system (the Panarea Automatic Monitoring Station – PAMS) represent a significant improvement over the earlier system installed at Trieste, in terms of robustness, data transfer, and system autonomy. A schematic outline of the system is given in Figure 2, whereby a central control unit located on-shore is responsible for power management (solar panels and batteries), data storage and transfer, and interrogation of the submarine sensors attached via cable. Data transfer is conducted in real-time via GPRS onto the internet, with a dedicated server installed on the modem card that allows for all monitoring parameters to be remotely checked using a web site. This configuration represents a drastic improvement for the remote control of the system, both in terms of flexibility and costs.

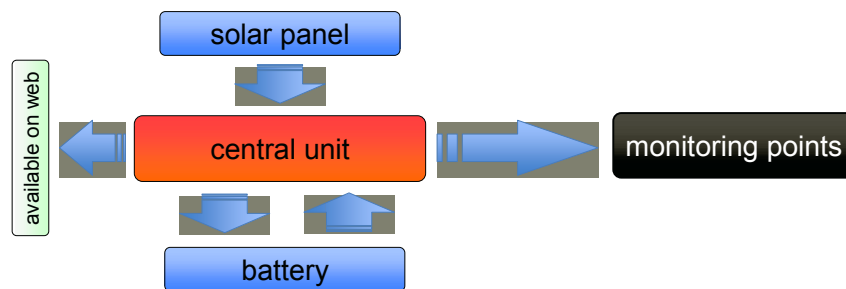


Figure 2. Flow chart of the PAMS system. 1. The central unit transforms and stores on the battery the energy provided by the solar panel. 2. The central unit changes the 12V DC input current to 24V DC to prevent a voltage drop along the 300m-long cable. 3. Each probe re-changes the variable input current to the operative 5V DC. 4. RS485 protocol is used for communication between the central unit and each probe. The twisted pair cable prevents data-loss in transmission. The entire system is controlled by an in-house designed software package

A total of 3 measurement points can be monitored via cable, with each point capable of hosting two autonomous sensor systems via “Y” splices (Fig. 3). The entire cable length is about 350m, with the locations of the three monitoring points selected on the basis of 2 emission points and one background point at the Panarea site. Whereas the design and functioning of the central control unit has remained constant throughout the development of this prototype, the sensor units created for sub-marine deployment have been modified due to the results observed during preliminary testing, as described below.

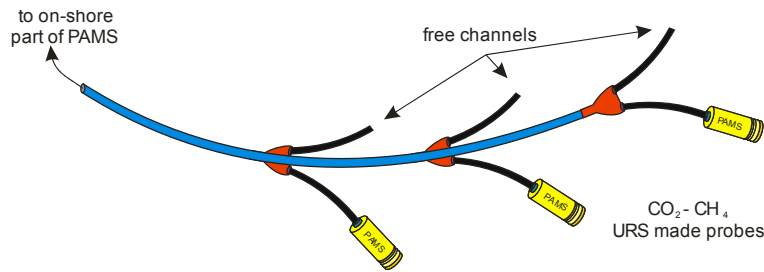


Figure 3. The PAMS system is able to monitor three different points with two autonomous sensors each. Three of these will be equipped with Sapienza-made probe for dissolved CO_2 and CH_4 analysis. The other three channels will be connected to the system developed by CO2ReMoVe partners BGR for the analyses of free gas. Submersed probes are connected by a 300 m long cable (twisted pair) in which 3Y splice junction allow the connection of the probes.

3.2. Initial sensor unit design and testing

Each sensor unit consisted of a single plastic housing containing a control card, a semi-conductor sensor for methane, a solid electrolyte sensor for carbon dioxide, and pressure and water temperature sensors. Clearly important issues related to the gas sensors include sensor warm-up time, response time, sensitivity, reproducibility, total lifetime and cost, and the listed sensors were chosen based on a compromise amongst these various criteria.

Considering that the measurement of the dissolved gases is done via gas diffusion through a semi-permeable membrane, the issue of response time (T_{90} – i.e. the time needed to reach 90% of a given concentration) coupled with sampling frequency becomes important. In this regard, the system is designed for long-term deployment and low-frequency sampling (twice per day), and thus sensors with slow response times were deemed acceptable because there would be sufficient time between sampling to allow for system equilibration. For this reason it was considered appropriate to use a semi-conductor sensor similar to those used in commercial probes for the methane measurements. The CO_2 electrolyte sensor was chosen primarily due to its low cost. Tests confirmed that both the range of measurement sensors selected and their sensitivity are appropriate for the measurement of the amount of dissolved gases present in the seawaters of Panarea.

Initial laboratory tests were aimed at quantifying sensor response and developing necessary correction factors for temperature and pressure (Fig. 4). A specifically designed test chamber was used for all calibrations which consists of an internal volume where the sensors are placed and where constant gas concentrations and pressures are

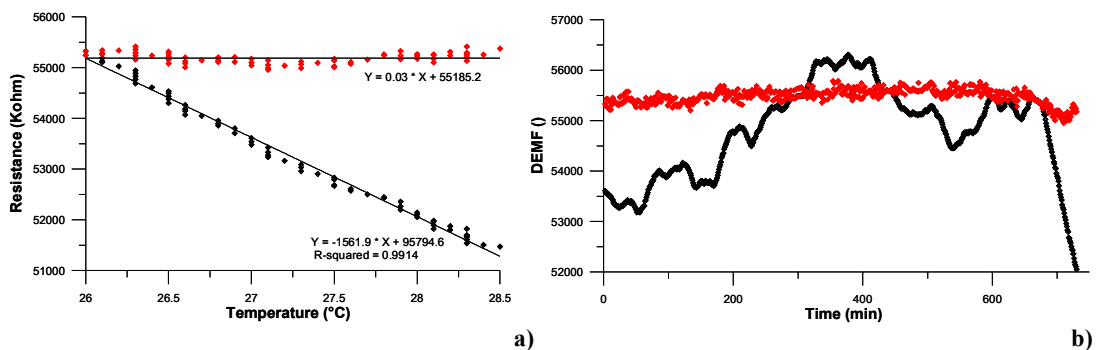


Figure 4. Different laboratory tests were carried out for the calculation of the response time and for correction of the temperature influence in order to obtain a “clean” signal before the calibration. Based on the coefficient found with the first plot (a) it was possible to correct the sensor signal (red line in plot b).

maintained. This is surrounded by a second volume in which flowing water is used to maintain a constant temperature in the internal chamber (Fig. 5). This tool has allowed us to make numerous tests by changing the temperature and pressure conditions and measurement environment (i.e. in air or in water).

Simulations were also conducted to test the stability and browser compatibility of the web site used for remote system management and data transfer. The final configuration of this web site is a graphically simple but powerful tool in which the data of the last PAMS acquisition is visible, and where it is possible to: i) perform password-enabled data download; ii) load the last image acquired by the system (remote webcam); and iii) find references to contact people who developed the system (Fig. 6).

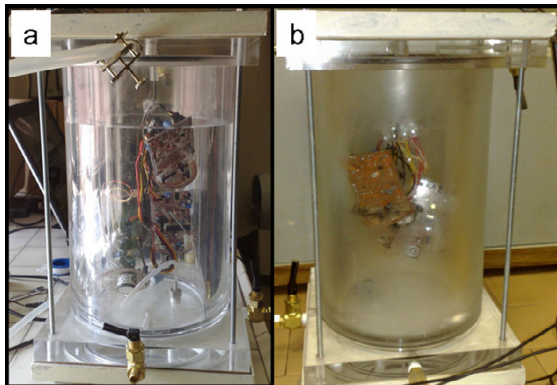


Figure 5. Boundary conditions during the laboratory test were changed using a specifically designed double room chamber. Figure a shows a environmental temperature experiment and figure b show the same test carried out at low temperature.

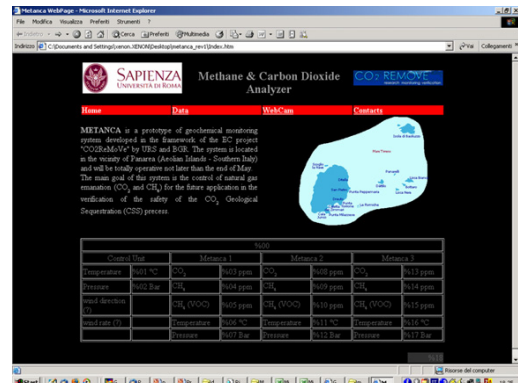


Figure 6. Remote control of the system is based on a web site interface. Using an internet connection it is possible to check and download acquired data and see the webcam images.

A preliminary deployment of this prototype station was performed near Panarea Island late in April 2008 using only a single measurement point; Figures 7 and 8 show some stages of system installation. Installation of the on-shore control unit immediately highlighted inconsistent GPRS signal quality at that location, as the original software design required a constant signal for system activation and data transfer. The test ended after only three days because of these communication problems and because some parameters returned inconsistent results. For example, although the CH₄ measurements seemed to be valid, the dissolved CO₂ analyses were not stable. This type of



Figure 7. The photos in this figure show a particular of the PAMS installation, an overall view from the Bottaro reef, the boat used for the installation and a gas vent occurring in the area.

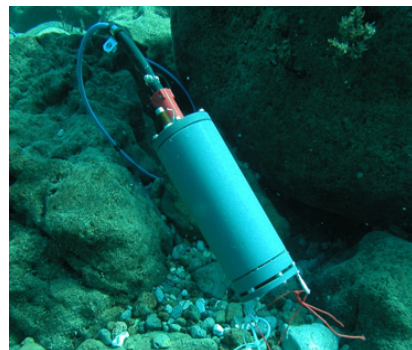


Figure 8. Probe installed into the waters of Panarea during the field test of April 2008.

response from the CO₂ sensor is linked to a known limitation of this technology that, when tested in situ, was probably amplified with respect to the laboratory tests. Based on the results obtained during the field test, it was decided to redesign some parts of the system to better adapt them to the in situ conditions.

3.3. Sensor modifications and testing

The decreasing of cost of NDIR sensors for measuring CO₂ concentrations made it feasible to use them in place of the less stable solid electrolyte sensors, thus maintaining the relatively low total cost of the system. The probes were totally redesigned to use this new type of sensor, and laboratory tests were started in July 2008 to observe the stability, response, and sensitivity of the new system. Results were extremely promising, suggesting that the types of problems encountered during the field trials should not occur again. In parallel, the start up procedure and data transfer protocols of the controlling software were modified so that even in the case of problems with GPRS coverage, it will still be possible to activate the PAMS. In addition to the benefits already described, the lower power consumption rates of the probes equipped with the NDIR sensors will allow for a higher measurement frequency (probably every two hours). Final calibration and laboratory testing are underway and on-site installation of the new system off Panarea Island is planned in the following weeks. The new installation will cover the complete version of the system, with all three measurement points active.

4. Data treatment (Trieste and Caimore monitoring systems)

At present there are no monitoring data available for the PAMS because of the problems described above. A small dataset will be available in the near future and this data will probably be incorporated into the final version of the proceedings. However, some examples of data collection and treatment can be shown using the results acquired by similar monitoring systems installed in the Gulf of Trieste and in the Caimore Plain, both of which have conducted long-term monitoring of dissolved CO₂ concentrations.

Figure 9 shows the data from the Trieste monitoring system. These results indicate how the commercial CH₄ sensor ceased to function after a relatively short deployment period, in contrast to the in-house system designed for CO₂ monitoring. Observed concentrations for both gases are comparable with the typical seawater values under similar conditions. Box plots constructed to test for potential concentration variations between data acquired during the day and the night do not show any appreciable difference (fig. 10).

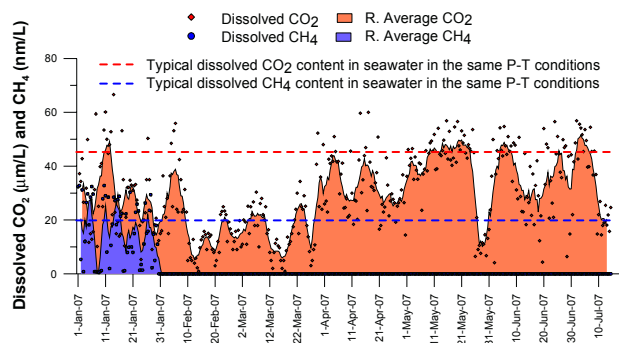


Figure 9. In general the Trieste monitoring system data show dissolved CH₄ and CO₂ concentration comparable with the typical values present in seawater in the same conditions. The commercial methane sensor ceased to function after January 2007.

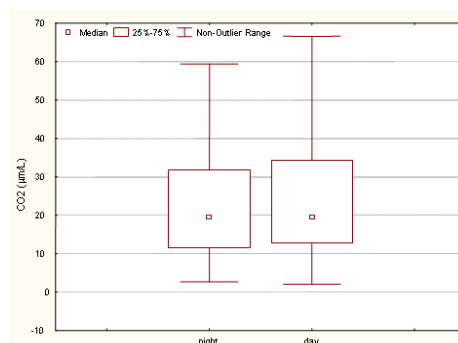


Figure 10. Box plots of the Trieste data show that no difference occurs between samples collected during the day and during the night.

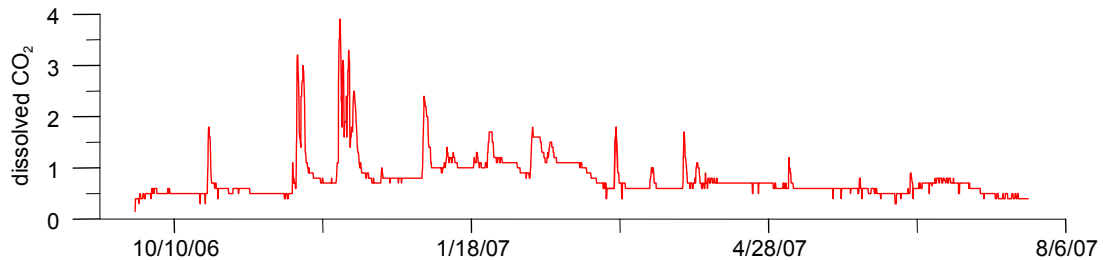


Figure 11. Dissolved CO₂ data acquired by the Camaiole monitoring system. These results show two clear anomalies and two potential anomalies, whereas all other peaks can probably be interpreted as background noise.

The Camaiole dataset (Fig 11) was collected from September 2006 to July 2007 and is sufficiently long enough to allow for time series analyses. Collected data were elaborated using the Auto-Correlation Function (ACF) and Cross-Correlation Function (CCF) techniques. ACF is used to transform the data into a stationary series (i.e. constant variance) to remove any serial correlation between adjacent data points and make them independent, and to forecast future behavior of the studied variables. Instead, CCF is a bivariate technique useful to study the serial behavior and time dependence between two variables. The ACF analysis of the CO₂ data highlights two peaks in correspondence of lags 113 (14 days) and 136 (17 days), indicating the presence of a cyclical component (Fig. 12). The CCF analysis was applied to the dissolved CO₂ data and earthquake events that occurred in the proximity of the monitoring system. This analysis highlights a positive, statistically-significant peak in correspondence of the positive lag 77 (about 9 days), indicating that the CO₂ signal occurs about 9 days before the earthquake (Fig. 13).

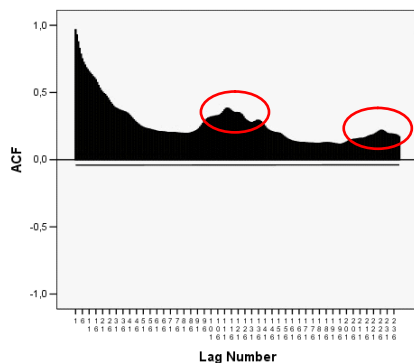


Figure 12. Auto-correlation function highlights the presence of a cyclical component.

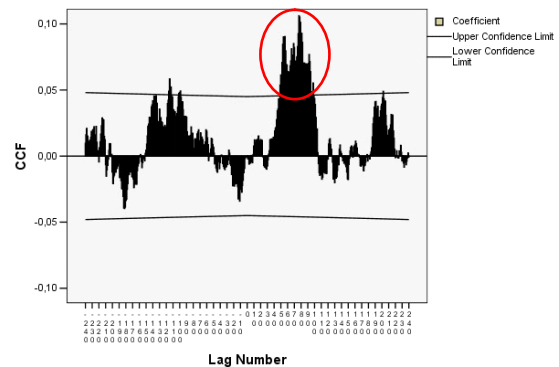


Figure 13. Cross-correlation function highlights the presence of positive peak in correspondence of the lag 77.

5. Conclusions

The monitoring of CO₂ geological storage sites will be a critical issue for the eventual wide-spread deployment of this climate change mitigation technique. Near-surface geochemical monitoring is particularly important, as it allows for a *direct assessment* of whether the injected CO₂ has migrated upward and is being transferred to the biosphere (i.e. surface water or atmosphere); this knowledge is needed to guarantee public safety and for carbon credit auditing. While discontinuous soil gas and CO₂ flux sampling (on-shore) or water sampling (off-shore) have the advantage of covering potentially large areas, they are limited by the cost of each individual survey, the

difficulty of assessing the results in terms of diurnal or seasonal variability, and the possibility of missing a leak in time (e.g. if a detectable leak occurs after a survey has been conducted). Geochemical monitoring stations overcome these problems by continuously sampling and analyzing samples, thus giving a complete dataset that can be analyzed statistically. While a station can only measure a single point, the decreasing costs of components and new, innovative designs will allow for networks of stations to be installed at strategic locations for a wider coverage. The results presented in this article show the potential for such stations, describing how in-house development and construction can greatly decrease costs and increase flexibility. Experience is needed, however, for the development of such stations in marine environments, where the corrosive nature of seawater, the potential for elevated hydrostatic pressures, and the fact that the measurement points are typically far from infrastructure or power supplies makes this work technically challenging. Finally, as a continuous monitoring station produces large quantities of data, statistical methods are needed interpret the results in terms of trends and correlations between measured parameters.

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